

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



A32

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>6</sup>: C04B 14/00, 14/10, 33/02, C09C 1/42</p>		A1	<p>(11) International Publication Number: <b>WO 97/30950</b> (43) International Publication Date: 28 August 1997 (28.08.97)</p>
<p>(21) International Application Number: PCT/US97/02706 (22) International Filing Date: 21 February 1997 (21.02.97)</p>		<p>(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, UZ, VN, YU, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p>	
<p>(30) Priority Data: 60/012,143 23 February 1996 (23.02.96) US</p>		<p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(71) Applicants: SOUTHERN CLAY PRODUCTS, INC. [US/US]; 1212 Church Street, Gonzales, TX 78629 (US). THE DOW CHEMICAL COMPANY [US/US]; 1790 Building, P.O. Box 1967, Midland, MI 48641-1967 (US).</p>			
<p>(72) Inventors: GONZALES, Antonio; P.O. Box 395, Moulton, TX 77975 (US). NICHOLS, Kevin, L.; 305 Rosemary Lane, Lake Jackson, TX 77566 (US). POWELL, Clois, E.; 336 Lake Ridge Drive, Seguin, TX 78155 (US).</p>			
<p>(74) Agent: RENDA, Barbara, L.; Klauber &amp; Jackson, 411 Hackensack Avenue, Hackensack, NJ 07601 (US).</p>			
<p>(54) Title: IMPROVED ORGANOCLAY COMPOSITIONS</p>			
<p>(57) Abstract</p> <p>Organoclay compositions which comprise the reaction product of a smectite-type clay having an ion exchange capacity of at least 50 meq. wt. per 100 g. clay (active basis), and mixture of a quaternary ammonium compound and a chain transfer agent which is a thiol, <math>\alpha</math>-methylketone, <math>\alpha</math>-methylalcohol or a halogen compound are useful agents for use in the processes for the preparation of thermoplastic materials.</p>			

## IMPROVED ORGANOCLAY COMPOSITIONS

BACKGROUND OF THE INVENTION

This invention relates generally to organoclays, and, more specifically, to improved 5 organoclays which are produced by the reaction of the organoclay with an chain transfer agent.

Organoclays, representing the reaction product of a smectite-type clay with a 10 quaternary ammonium compound, have long been known for use in gelling of organic liquids such as lubricating oils, linseed oil, toluene and the like. A large variety of highly useful products, such as lubricating greases, are producible through use of such gelling agents. The procedures and chemical reactions pursuant to which these organoclays are prepared, are well-known. Thus, under appropriate 15 conditions, the organic compound which contains a cation, will react by ion exchange with the clay which contains a negative layer lattice and exchangeable cations to form the organoclay products.

Other uses for such modified organoclays are those such as are disclosed in U. S. Patent 5,151,155, wherein organically modified smectite clays are utilized in a 20 process for deinking wastepaper, and in U. S. Patent 4,677,158, wherein smectite-type clays which have been reacted with quaternary ammonium compounds are utilized as thickeners for aqueous suspensions, particularly latex paints and caulk. These modified organoclays differ from those of the present invention in the type of 25 the agent with which they are intercalated. This modification produces organoclays with properties which make them suitable for use in the manufacture of thermoplastics.

OBJECTS OF THE INVENTION

30 It is an object of the present invention to prepare organoclay compositions having properties making them useful for the manufacture of thermoplastic compositions.

FIGURE 4 is a d-spacing tracing of a montmorillonite clay intercalated with 80 mer dimethyl-di-hydrogenated tallow ammonium chloride (2M2HT) and 20 mer dimethylaminomethacrylate "Q" salt methyl chloride.

5

### DESCRIPTION OF PREFERRED EMBODIMENTS

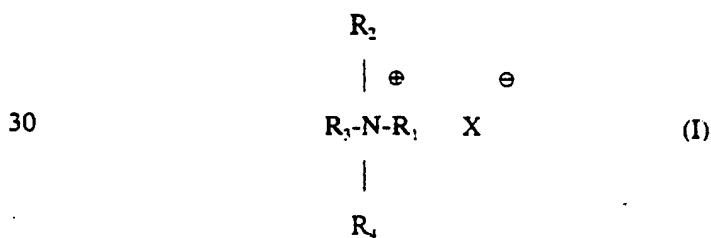
The smectite clays which are utilized as one of the starting materials of the present invention are those which have been conventionally utilized in the prior art.

Suitable smectite-type clays are those which have a cation exchange capacity of at 10 least 50 milliequivalents (meq.) weight (wt.) per 100 grams of clay (active basis).

Useful clays for such purposes include the naturally occurring Wyoming variety of swelling bentonite and similar clays, and hectorite, which is a swelling magnesium-lithium silicate clay. The clays are preferably converted to the sodium form if they are not already in this form. This can be effected, again as is known in the art, by 15 a cation exchange reaction, or the clay can be converted via an aqueous reaction with a soluble sodium compound.

Smectite-type clays prepared synthetically can also be utilized, such as montmorillonite, bentonite, beidelite, hectorite, saponite, and stevensite. Such 20 clays, and processes for their preparation, are described in U. S. Patents 4,695,402, 3,855,147, 3,852,405, 3,844,979, 3,844,978, 3,671,190, 3,666,407, 3,586,478, and 3,252,757, all of which are herein incorporated by reference.

The quaternary ammonium compounds which can be utilized in the compositions of 25 the present invention are known agents typically utilized in the preparation of organoclays and include alkyl ammonium compounds of the formula:



Substituted benzyl moieties, such as would be derived from ortho-, meta- and para-chlorobenzyl halides, para-methoxybenzyl halides, ortho-, meta and para-nitrilobenzyl halides, and ortho-, meta and para-alkylbenzyl halides wherein the alkyl chain contains from 1 to 22 carbon atoms; and fused ring benzyl-type

5 moieties, such as would be derived from 2-halomethylnaphthalene, 9-halomethylanthracene and 9-halomethylphenanthrene, wherein the halo group would be defined as chloro, bromo, iodo, or any other such group which serves as a leaving group in the nucleophilic attack of the benzyl type moiety such that the nucleophile replaces the leaving group on the benzyl type moiety.

10 Examples of aryl groups would include phenyl such as in N-alkyl and N, N-Dialkyl anilines, wherein the alkyl groups contain between 1 to 22 carbon atoms; ortho-, meta and pre-nitrophenyl, ortho-, meta- and para-alkyl phenyl, wherein the alkyl group contains between 1 and 22 carbon atoms, 2-, 3-, and 4-halophenyl

15 wherein the halo group is defined as chloro, bromo, or iodo, and 2-, 3-, and 4-carboxyphenyl and esters thereof, where the alcohol of the ester is derived from an alkyl such as carbon atoms, aryl such as phenol, or aralkyl such as benzyl alcohols; fused ring aryl moieties such as naphthalene, anthracene, and phenanthrene.

20 The  $\beta, \gamma$ -unsaturated alkyl group may be selected from a wide range of materials. These compounds may be cyclic or acyclic, unsubstituted or substituted with aliphatic radicals containing up to 3 carbon atoms such that the total number of aliphatic carbons in the  $\beta, \gamma$ -unsaturated radical is 6 or less. The  $\beta, \gamma$ -unsaturated alkyl radical may be substituted with an aromatic ring that likewise is conjugated

25 with the unsaturation of the  $\beta, \gamma$ -moiety or the  $\beta, \gamma$ -radical is substituted with both aliphatic radicals and aromatic rings.

Representative examples of cyclic  $\beta, \gamma$ -unsaturated alkyl groups include 2-cyclohexenyl and 2-cyclopentenyl. Representative examples of acyclic  $\beta, \gamma$ -unsaturated alkyl groups containing 6 or less carbon atoms include propargyl; allyl(2-propenyl); crotyl(2-butenyl); 2-pentenyl; 2-hexenyl; 3-methyl-2-but enyl; 3-

The salt anion of the ammonium salt may be methosulfate, ethosulfate, methylcarbonate, ethylcarbonate, chloride, bromide, or mixtures thereof, and is most preferably a methosulfate ion. The salt anion may also, however, be nitrate, hydroxide, acetate, or mixtures of these.

5

Illustrative of the numerous patents which describe organic cationic salts, their manner of preparation and their use in the preparation of organophilic clays are commonly assigned U.S. Pat. Nos. 2,966,506, 4,081,496, 4,105,578, 4116,866, 4,208,218, 4,391,637, 4,410,364, 4,412,018, 4,434,075, 4,434,076, 4,450,095 and 4,517,112, the contents of which are incorporated by reference.

10

The quaternary ammonium compound which contains a carbon-carbon double bond for the free radiacal polymerization can be any of the above-described compounds of formula I which contain the necessary double bond. In a preferred embodiment, 15 the organoclay of the present invention thus contains two different types of quaternary ammonium compounds. Alternatively, a chain transfer agents can be included in place of the second quaternary compound. These include thiols, for example DL-cysteine,  $\alpha$ -methylketones, such as acetone,  $\alpha$ -methylalcohols, such as isopropanol, or halogen compounds, such as chloroform and carbon tetrachloride. 20 Particularly useful, due to its efficiency in chain transfer processes, is DL-cysteine.

25

The chain transfer agent present in combination with the quaternary ammonium salt in the organoclays of the present invention determine the particularly advantageous properties of the resultant organoclays of the present invention. Thus, the incorporation of the chain transfer agents with the quaternary ammonium compound provide modified organoclays which can be directly utilized in the process for the preparation of thermoplastics, and particularly polystyrene and high impact polystyrene materials.

30

Highly preferred embodiments of the present invention are organoclays which comprise the reaction product of smectite-type clays with a mixture of a quaternary

A further embodiment of the present invention is the process for preparing the organoclay composition comprising the reaction product of a smectite-type clay having an ion exchange capacity of at least 50 meq. wt. per 100g. clay (active basis), and a mixture of a quaternary ammonium compound and a chain transfer agent which comprises:

5 a) dispersing a smectite type clay having an ion exchange capacity of at least 50 meq. wt. per 100 g. clay in an aqueous media;

10 b) heating the dispersing of step (a) to a temperature in excess of 30° C;

c) adding the heated dispersion of step (b) of the quaternary ammonium salt, in the desired milliequivalent ratio;

15 d) adding the mixture of step (c) to a solution of the chain transfer agent, pretreated with a strong mineral acid, if necessary; and

e) agitating the mixture of step (d) to effect completion of the reaction.

20 The organoclay composition of the present invention is thus prepared by admixing an aqueous dispersion of the smectite-type clay, warmed to a temperature in excess of 30° C., with a quaternary ammonium compound and the chain transfer agent to exchange the metal counterions that are naturally present in the smectite-type clay. The reaction is typically conducted at a temperature within the range of from about 25 40° C. to about 100 °C. for a period of time sufficient for the quaternary ammonium compound and the chain transfer agent to react with the clay particles.

Preferably, the clay is dispersed in the water at a concentration from about 3% to about 15% by weight and the slurry is centrifuged to remove non-clay impurities.

30 The slurry is then agitated and heated to the desired temperature, and the quaternary ammonium salt added in the desired milliequivalent ratio. To this mixture is then added the chain transfer agent which has, if necessary, been pretreated, typically by

equipment, bottles, containers, components for the electrical and electronics industries, car components, circuits, fibers, semi-finished products which can be shaped by machining and the like. The use of the materials for coating articles by means of powder coating processes is also possible, as is their use as hot-melt 5 adhesives.

These molding compositons can also be used in the production of sheets and panels having valueable properties. Such sheets and panels may be shaped by conventional processes such as vacuum processing or by hot pressing to form useful objects.

- 10 The sheets and panels are also suitable as coating materials for other materials comprising, for example, wood, glass, ceramic, metal or other plastics, and outstanding strengths can be acheived using conventional adhesion promoters, for example, those based on vinyl resins. The sheets and panels can also be laminated with other plastic films and this is preferably effected by coextrusion, the sheets 15 being bonded in the molten state. The surfaces of the sheets and panels, including those in the embossed form, can be improved or finished by conventional methods, for example by lacquering or by application of protective films.

These polymer composites are also useful for fabrication of extruded films and film 20 laminates, as for example, films for use in food packaging. Such films can be fabricated using conventional film extrusion tecniue.

The invention will now be illustrated by a series of Examples, which are intended to set forth typical and preferred procedures to be utilized in the practice of the 25 invention.

#### EXAMPLE 1

The preparation of a smectite-type clay composition comprising the reaction product 30 of a smectite-type clay and a quaternary ammonium compound (80 mer) and a chain transfer agent (10 mer) is prepared as follows:

about 10 minutes. Then, the mixture is again filtered, fluid bed dried at a temperature of about 80°C., and milled on a .2 mm screen to afford a montmorillonite clay intercalated with 80 mer dimethyl-di-hydrogenated tallow ammonium chloride and 20 mer DL-cysteine, with a d-spacing tracing as shown in 5 Figure 2.

### EXAMPLE 3

Repetition of the procedure detailed in Example 1, using 80 mer dimethyl-di-10 hydrogenated tallow ammonium chloride and 10 mer N,N-dimethylaminoethylmethacrylate "Q" salt methyl chloride afforded a montmorillonite clay intercalated with 80 mer dimethyl-di-hydrogenated tallow ammonium chloride and 10 mer N,N-dimethylaminoethylmethacrylate "Q" salt methyl chloride, with a d-spacing tracing as shown in Figure 3.

15

### EXAMPLE 4

Repetition of the procedure detailed in Example 1, using 80 mer dimethyl-di-10 hydrogenated tallow ammonium chloride and 20 mer N,N-dimethylaminoethylmethacrylate "Q" salt methyl chloride afforded a montmorillonite clay intercalated with 80 mer dimethyl-di-hydrogenated tallow ammonium chloride and 20 mer N,N-dimethylaminoethylmethacrylate "Q" salt methyl chloride, with a d-spacing tracing as shown in Figure 4.

25

1           4. The composition according to Claim 2 wherein the quaternary  
2 ammonium compound is dimethyl-di-hydrogenated tallow ammonium chloride and  
3 the chain transfer agent is DL-cysteine.

5. A process for the preparation of an organoclay composition comprising the reaction product of a smectite-type clay having an ion exchange capacity of at least 50 meq. wt. per 100 g. clay (active basis), and mixture of a quaternary ammonium compound with either another quaternary ammonium compound containing a carbon-carbon double bond, or a chain transfer agent which is a thiol,  $\alpha$ -methylketone,  $\alpha$ -methylalcohol or a halogen compound, which comprises:

8 a) dispersing a smectite-type clay having an ion exchange capacity of at least  
9 50 meq. wt. per 100 g. clay, in an aqueous media;

11 b) heating the dispersion of step (a) to a temperature in excess of 30° C;

c) adding to the heated dispersion of step (b) of a quaternary ammonium salt, in the desired milliequivalent ratio:

15  
16 d) adding the mixture of step (c) to a solution of the chain transfer agent,  
17 pretreated with a strong mineral acid, if necessary; and

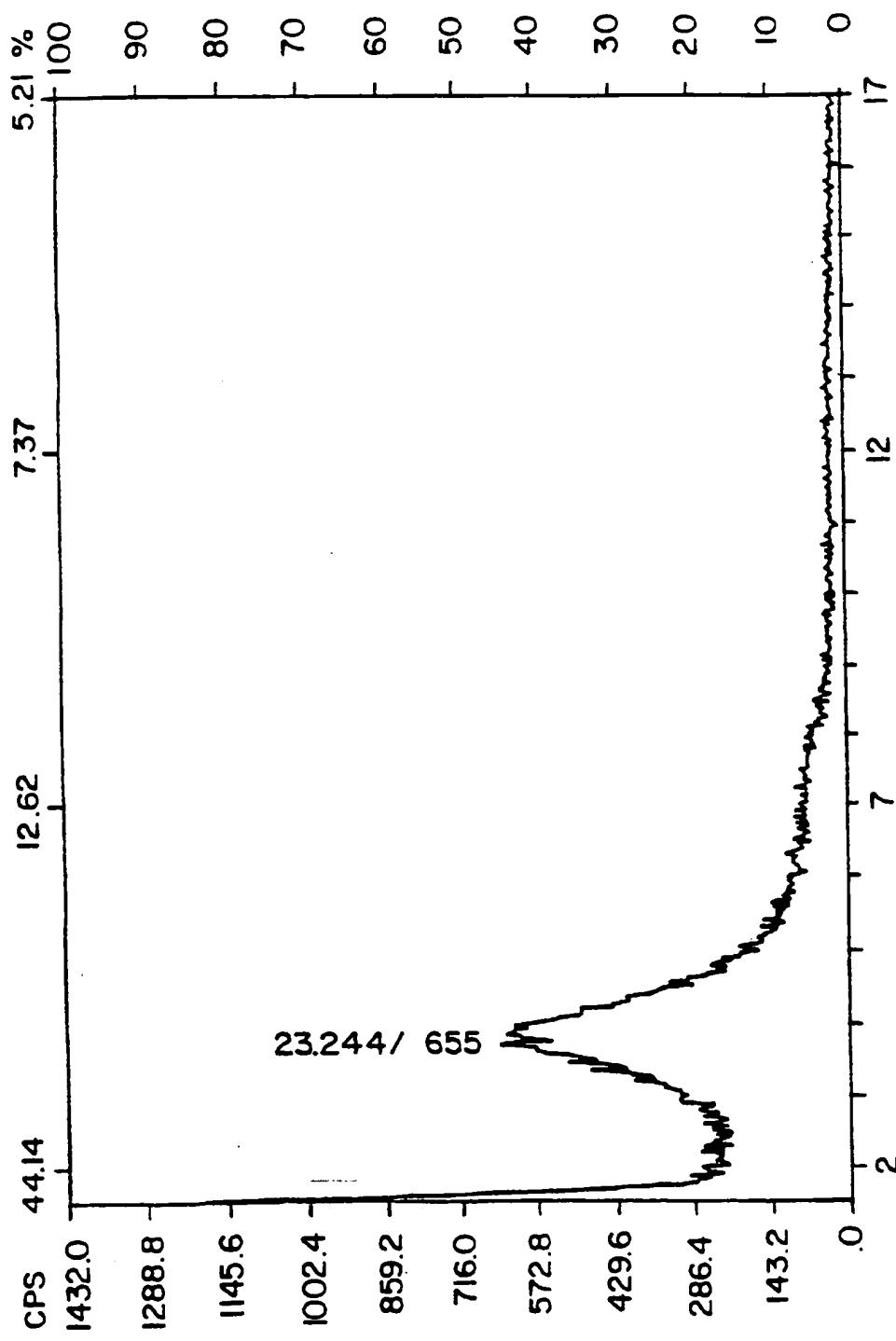
19 e) agitating the mixture of step (d) to effect completion of the reaction.

1        6. The process according to Claim 5 wherein the quaternary ammonium  
2 compound of formula I has the formula

$$\begin{array}{c}
 4 & & R_2 \\
 5 & | & \oplus & e \\
 6 & R_3-N-R_1 & X & (I) \\
 7 & | \\
 8 & R_4
 \end{array}$$

1 / 4

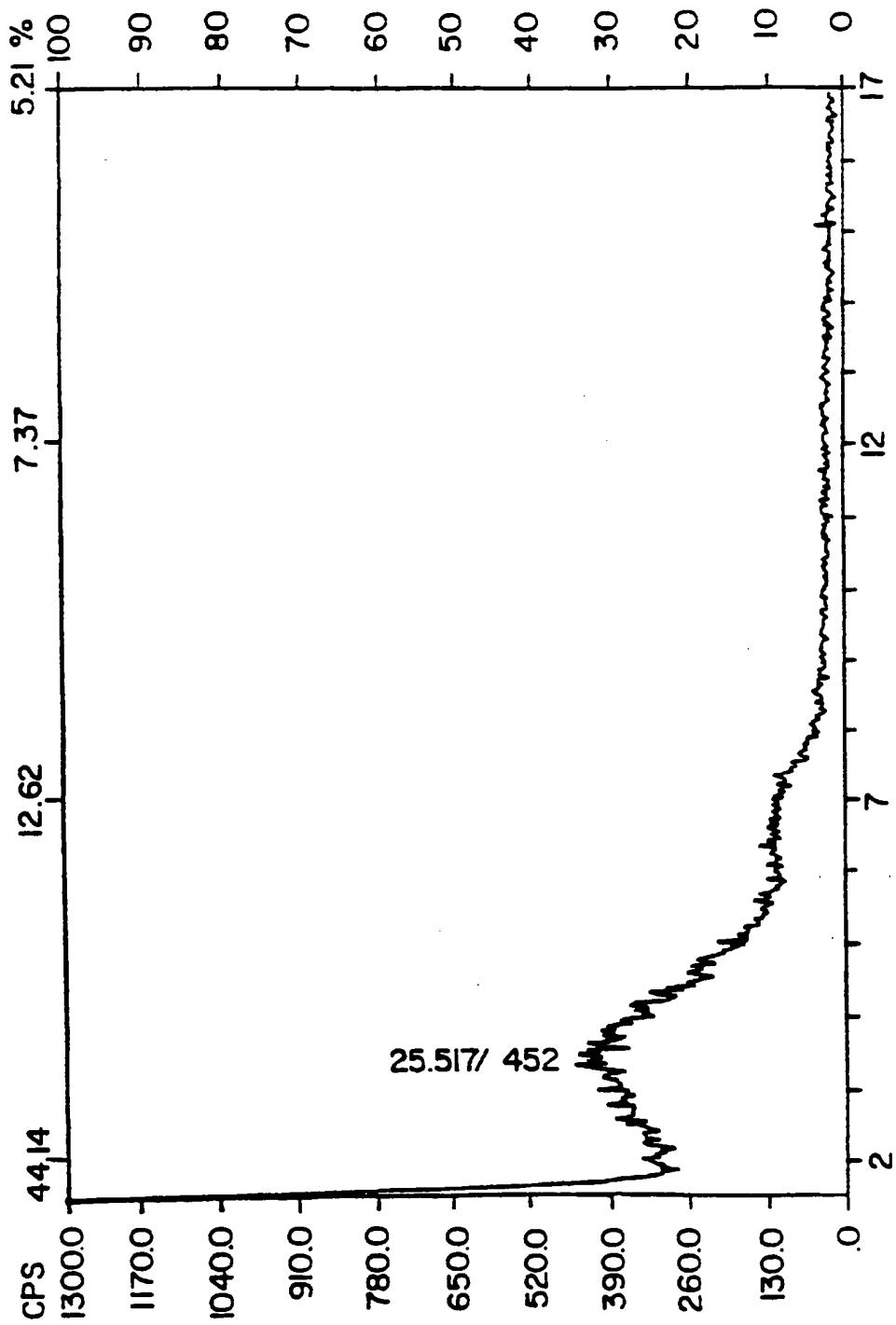
FIG. 1



SUBSTITUTE SHEET (RULE 26)

3 / 4

FIG.3



SUBSTITUTE SHEET (RULE 26)

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/02706

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C04B 14/00, 14/10, 33/02; C09C 1/42  
US CL :106/486, 487, 287.17; 501/148; 252/315.2

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 106/486, 487, 287.17; 501/148; 252/315.2  
IPC(6): C04B 14/00, 14/10, 33/02Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
noneElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
none

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,425,244 A (HOUSE) 10 JANUARY 1984, SEE COLUMN 3, LINE 53-COLUMN 9, LINE 61.	1,2
Y	US 5,429,999 A (NAE ET AL.) 04 JULY 1995, SEE THE CLAIMS.	1-6
Y	US 4,743,305 A (DOIDGE ET AL.) 10 MAY 1988, SEE COLUMN 1, LINE 2-COLUMN 2, LINE 36 AND THE EXAMPLES.	1,2,5,6

 Further documents are listed in the continuation of Box C.  See patent family annex.

* Special categories of cited documents:	
*A* document defining the general state of the art which is not considered to be of particular relevance	" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*B* earlier document published on or after the international filing date	"* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*L* document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another claim or other special reasons (as specified)	"* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*O* document referring to an oral disclosure, use, exhibition or other source	"* document member of the same patent family
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

09 APRIL 1997

Date of mailing of the international search report

11 JUL 1997

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231Authorized officer  
*Michael L. V. M.*  
MICHAEL MARCHESSI  
Telephone No. (703) 308-0661

Facsimile No. (703) 305-3230

Form PCT/ISA/210 (second sheet)(July 1992)\*